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AUTHOR(S):

Kobayashi, Takashi; Isoda, Seiji

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## Epitaxial Growth and Polymorphism of Phthalocyaninato-Thorium

Takashi KOBAYASHI\* and Seiji ISODA\*

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Thin films of Th-phthalocyanine made by vacuum deposition on KCl were studied by electron microscopy. The formation of a new polymorph was found and its structure and epitaxial relation to the substrate have been revealed.

KEY WORDS: Epitaxy/Th-phthalocyanine/Crystal structure/Polymorphism

### INTRODUCTION

Among many phthalocyanine metal-derivatives, actinoid derivatives, such as uranium- or thorium- di-phthalocyanine ( $\text{MPC}_2$ ,  $\text{M}=\text{U}$  or  $\text{Th}$ ) have firstly been found to form as the sandwich-type molecule<sup>1)2)3)</sup> in which a eight coordinating metal ion is placed between two Pc ligands. During the study of epitaxial growth of various kinds of organic materials, it has become clear that  $\text{Th-Pc}_2$  forms a well oriented epitaxial film which is assigned to a new polymorphic crystal. In the present paper the structure of the new polymorph and the epitaxial relationship between the film and the substrate are reported on the basis of the electron diffraction patterns and of the high resolution electron micrographs on which regular molecular arrangements and also many kinds of irregular ones<sup>4)</sup> can be observed.

### EXPERIMENTAL

The  $\text{ThPc}_2$  was synthesized by heating a stoichiometric mixture of Th metal powder and pure o-phthalodinitrile at about 350°C for several hours. The Th powder was washed with 1.0N HCl before the mixing and the o-phthalodinitrile was purified by sublimation method in air. The crude product was washed with acetone for 12 hours in Soxhlet extractor and then sublimed at 550°C under reduced  $\text{N}_2$  gas pressure. The crystalline product thus obtained was evaporated from a quartz crucible in a vacuum of  $2 \times 10^{-6}$  torr and deposited onto a (001) of a substrate KCl single crystal kept at 200°C. The substrate was preheated at 550°C for two hours in the vacuum in order to eliminate surface contaminant. The film thickness was monitored with a quartz microbalance to be 200 Å or less than 100 Å. These thicker and the thinner specimens were used for electron diffraction and for high resolution electron microscopy, respectively.

\* 小林 隆史, 磯田 正二: Laboratory of Crystal and Powder Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, JAPAN

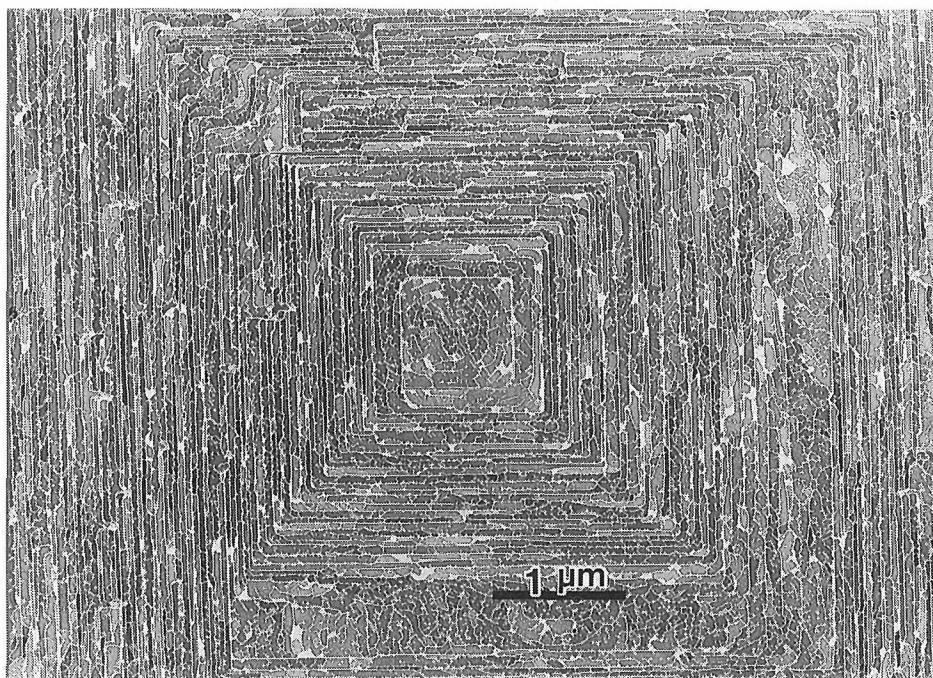


Fig. 1 ThPc<sub>2</sub> grown on KCl (001) plane.

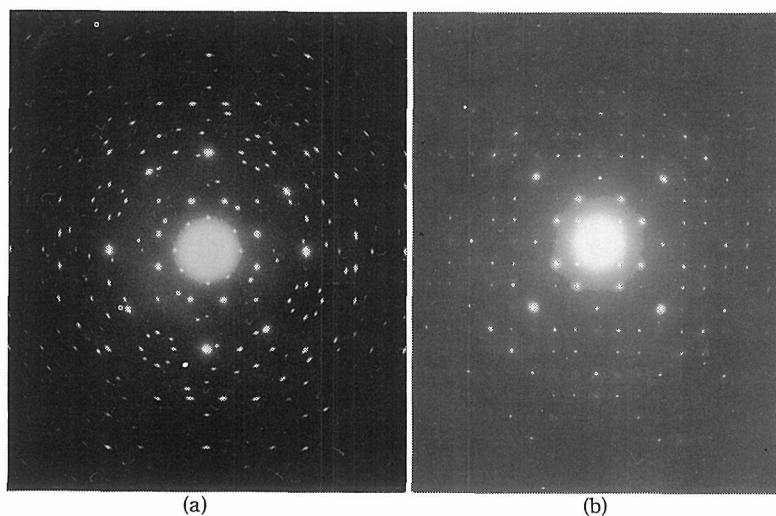


Fig. 2 Selected area electron diffraction patterns of ThPc<sub>2</sub> grown on KCl from relatively wide area showing a double orientation (a) and from a small area exhibiting a single orientation (b).

## RESULTS AND DISCUSSION

An electron micrograph of a film of ThPc<sub>2</sub> grown on KCl is reproduced in Fig. 1. As is evident from this micrograph, the film is composed of many small crystallites whose mean size is about several hundred angstrom or less in length. Their growth

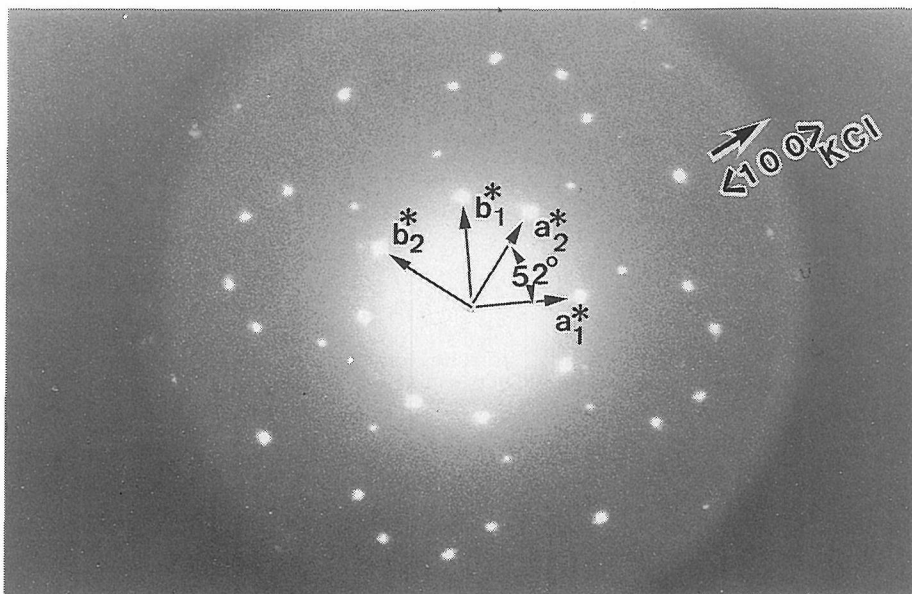


Fig. 3 Orientational relationship between two tetragonal lattices of ThPc<sub>2</sub> and the substrate.

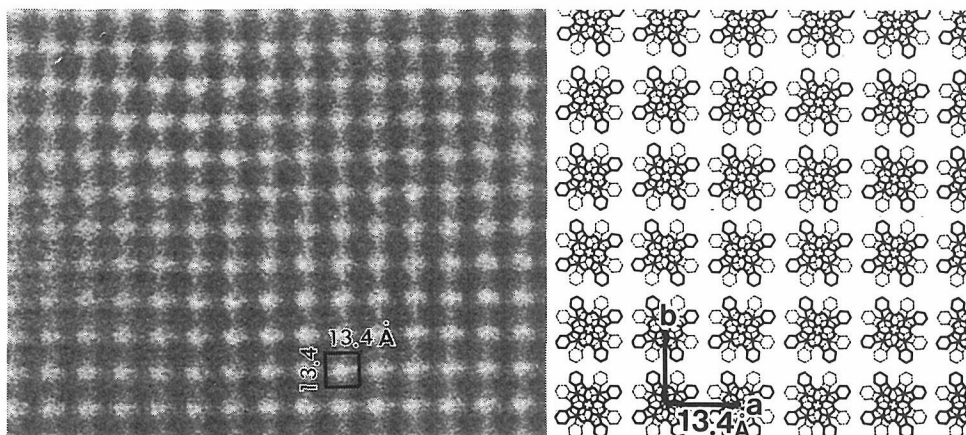


Fig. 4 High resolution electron micrograph of ThPc<sub>2</sub> shown in Fig. 1 and its model.

seems to be controlled by a surface structure of the substrate. The square frames along which the crystallites are arranged correspond to the surface steps of KCl produced by thermal etching caused by the preheat treatment of the KCl in vacuum. A selected area electron diffraction pattern from this epitaxial film is shown in Fig. 2(a), in which two single crystal patterns are superimposed with mutual positions rotated by 52° or 38° to each other. This relationship is illustrated in Fig. 3 where only the inner part of the pattern is reproduced for the simple interpretation. The direction of the crystal axis of KCl is also indicated by an arrow. When the smaller area of the specimen was selected, the individual patterns were isolated, clearly exhibiting a tetragonal symmetry with a

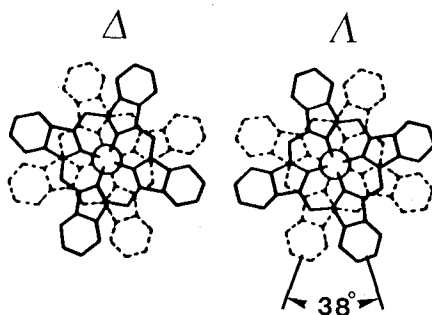


Fig. 5 Molecular structure showing the two isomers of  $\text{ThPc}_2$ .

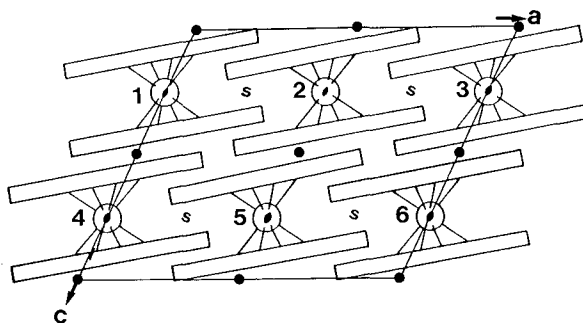


Fig. 6 A projection of  $\text{ThPc}_2$  crystal in the monoclinic form along the  $b$ -axis and symmetry elements in the unit cell.

periodicity of  $1/13.40 \text{ \AA}$  as shown in Fig. 2(b). This periodicity is tentatively taken as the unit length of the  $a^*$ - and  $b^*$ -axes for the tetragonal crystal. A high resolution electron micrograph of the same film is shown in Fig. 4(a) with its model (b) which also exhibits the molecular arrangement of the tetragonal symmetry. On the other hand, the molecular and single crystal structures of  $\text{ThPc}_2$  obtained by sublimation method were revealed by x-ray diffraction analysis. The crystal belongs to a space group of a monoclinic form (space group  $C2/c$ ) which is isomorphic with those of Uranium (IV) di-phthalocyanine and has the following lattice constants,  $a=18.92$ ,  $b=18.81$ ,  $c=15.92 \text{ \AA}$  and  $\beta=116^\circ$ . Therefore, the epitaxial film can be concluded to be composed of crystallites of a different polymorph of  $\text{ThPc}_2$ . The molecule in the monoclinic form revealed by x-ray diffraction method is composed of an eight-coordinating Th-atom sandwiched with two phthalocyanine macrorings which, being separated by a distance of about  $3.5 \text{ \AA}$ , mutually rotate by  $38^\circ$  around the normal axis as illustrated in Fig. 5. This molecule has no mirror symmetry or no inversion center as a whole, as is evident from the figure. On the contrary, the crystal lattice belonging to the space group of monoclinic  $C2/c$  has the symmetry elements of glide plane or inversion center. The molecular stacking of  $\text{ThPc}_2$  in the monoclinic crystal is schematically drawn as a  $b$ -axis projection in Fig. 6, the molecules 1 and 4 are, for example, related by a glide plane  $c(x \ 0 \ z)$  or  $c(x \ 0.5 \ z)$ . This means that two pairs of sandwich type molecules

related by mirror symmetry co-exist in the crystal. Two molecular configurations are shown in Fig. 5 which are the molecular isomers designated as  $\Lambda$ - and  $\Delta$ -forms. If the molecular site 1 is occupied by the  $\Lambda$ -form, the sites 2 and 3 also should be occupied by the  $\Lambda$ -form and the 4,5 and 6 are by the  $\Delta$ -form. In the case where the rotation angle of one ligand relative to the other is  $45^\circ$ , no such isomers exist and the molecule has mirror symmetries on planes through the Th(IV) vertical to the molecular plane. The molecular structure itself in the tetragonal polymorph is reasonably considered to be identical to that in the monoclinic form expecting easily from the structural characteristics of many other phthalocyanine derivatives. Therefore, the same stacking situation is expected where the  $\Lambda$ - and the  $\Delta$ -forms are stacked alternately in the tetragonal form. In order to achieve such a stacking the size of the tetragonal unit lattice should be twice or more as large as  $13.4 \times 13.4 \text{ \AA}^2$  if one restricts the discussion to two dimensional lattice packing. For example, a face-centred lattice of  $2a \times 2b$  can contain two sandwich type molecules in the unit cell. When one take the third dimension, i.e. the c-axis length, into consideration, the unit cell of  $a=b=13.4 \text{ \AA}$  is permissible making the c-dimension of about  $7 \text{ \AA}$  which is the size of the sandwich type molecule in the perpendicular direction to the molecular plane longer than  $14 \text{ \AA}$  which is twice the size of the sandwich type molecule. In the former case the molecular images on the ab-plane are identical. In the latter case the images of the projection along the c-axis become the superimposed one of the  $\Lambda$ - and  $\Delta$ -forms. However, the discriminating the superimposed or the respective molecular images is impossible at the present resolution of  $2.0 \text{ \AA}$ . Three dimensional electron diffraction study may decide the real structure of such thin small crystalline specimen as the present case.

The crystal a- or b-axis of the new polymorph takes a rigid orientation relative to the surface lattice of the substrate KCl. That is, the a-axis of the  $\text{ThPc}_2$  in the epitaxial film makes an angle of  $26^\circ$  toward clockwise or anticlockwise direction from the a- or b-axis of KCl as shown in Fig. 3. This axial correlation between a deposited organic crystalline film and a substrate alkali halide is often observed for tetragonal crystallite of other di-phthalocyanines or poly-phthalocyanines. For example, germanium oxy-phthalocyanine polymer crystal<sup>5)</sup>, various lanthanoid phthalocyanine derivatives<sup>6),7)</sup> or also some porphyrine derivatives<sup>8)</sup> grown on KCl or NaCl show the same orientational relationship with the crystal axis of the alkali halide substrate. There is an argument<sup>9)</sup> as to whether these orientational relationships between these phthalocyanines and the substrates are regulated by lattice misfit or by molecular registry of the first fixed molecule on the substrate surface. The conclusion for this argument is not drawn yet and will be reported in future. We can present an example of epitaxy<sup>10)</sup> to strengthen a general rule for tetragonal phthalocyanines to crystallize epitaxially on alkali halides with an angle of  $26^\circ$  to the a-axis of the substrates.

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